Observation of minority spin character of the new electron doped manganite $La_{0.7}Ce_{0.3}MnO_3$ from tunneling magnetoresistance

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We report the magnetotransport characteristics of a trilayer ferromagnetic tunnel junction build of an electron doped manganite ($La_{0.7}Ce_{0.3}MnO_3$) and a hole doped manganite ($La_{0.7}Ca_{0.3}MnO_3$). At low temperatures the junction exhibits a large positive tunneling magnetoresistance (TMR), irrespective of the bias voltage. At intermediate temperatures below T_C the sign of the TMR is dependent on the bias voltage across the junction. The magnetoresistive characteristics of the junction strongly suggest that $La_{0.7}Ce_{0.3}MnO_3$ is a minority spin carrier ferromagnet with a high degree of spin polarization, i.e. a transport half metal.

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There has been a lot of interest recently in the hole doped rare-earth manganites, where the rare-earth in the insulating parent compound is partially replaced by a divalent cation (such as Ca, Ba, Sr, Pb etc.) [1]. Around 30% hole doping most of these compounds such as $La_{0.7}Ca_{0.3}MnO_3$, $La_{0.7}Ba_{0.3}MnO_3$ have a half-metallic ferromagnetic ground state with a large magnetoresistance (MR) associated with the ferromagnetic transition temperature. Conversely, doping electrons by substituting the rare-earth atom by tetravalent Ce also drives the system into a ferromagnetic metallic ground state [2, 3, 4]. Unlike the hole doped compound where manganese is in a mixture of Mn^{3+} and Mn^{4+} valence states the tetravalent Ce drives the compound in a mixture of Mn^{3+} and Mn^{2+} valencies. The presence of Mn^{2+}/Mn^{3+} valencies induced by electron doping in $La_{0.7}Ce_{0.3}MnO_3$ was confirmed recently [5]. There exists an inherent symmetry between Mn^{4+} and Mn^{2+} as both are non Jahn-Teller ions, whereas Mn^{3+} is a Jahn-Teller ion. Moreover, $La_{0.7}Ca_{0.3}MnO_3$ and $La_{0.7}Ce_{0.3}MnO_3$ both have a Curie temperature of $T_C \approx 250$ K.

Beyond the phenomenon of colossal MR, novel properties arising from the interplay of spin, charge and orbital coupling and the competition of closely related energy scales make the manganites potential candidates for novel electronic devices. Devices exhibiting both large positive and negative MR have been fabricated by integrating doped manganites with other oxide ferromagnets. More recently rectifying characteristics could be demonstrated in $La_{0.7}Ce_{0.3}MnO_3/SrTiO_3$(STO)/$La_{0.7}Ca_{0.3}MnO_3$ tunnel junctions [6] and Nb-STO/(La,Ba)MnO_3 junctions [7]. However, a detailed understanding of the spin dependent electronic structure of these materials is important to exploit the complete potential of these compounds.

In this paper we report the magnetotransport properties of a $La_{0.7}Ce_{0.3}MnO_3$/STO($\approx$50Å)/$La_{0.7}Ca_{0.3}MnO_3$ tunnel junction grown onto conducting 0.5% Nb doped $SrTiO_3$ (Nb-STO) single crystalline substrate through pulsed laser deposition, whose fabrication has been reported earlier [6]. The device structure is illustrated in the inset of Fig. 1(a). The Nb-STO substrate acts as a conducting underlayer allowing us to measure the transport properties of the tunnel junction with current perpendicular to plane (CPP) geometry. In contrast to the hole doped compounds not much work [8, 9] could so far be done to understand the electronic structure of $La_{0.7}Ce_{0.3}MnO_3$. A major experimental obstacle stems from the fact that $La_{0.7}Ce_{0.3}MnO_3$ has so far been synthesized in single phase only in thin film form through high-energy pulsed laser deposition [4]. This is a restriction on many of the conventional probes and calls for alternative ways to extract information regarding the spin polarized electronic structure in these materials. Towards this end we have used magnetotransport properties of tunnel junctions comprising of two ferromagnetic electrodes separated by a thin insulating tunnel barrier. Most importantly, we wanted to establish whether this electron doped ferromagnet has minority spin carriers (MISC) (where the magnetization is antiparallel to the spin) or majority spin carriers (MASC) (magnetization parallel to the spin) at the Fermi energy E_F. The resistance across such a ferromagnetic tunnel junction (FTJ) depends on the relative orientation of the spins at E_F in the two electrodes. In zero field the magnetizations of the two ferromagnetic electrodes in an ideal FTJ are predominantly antiparallel owing to magnetostatic interaction between the ferromagnetic layers with in-plane magnetization. With the application of a magnetic field the magnetizations become parallel. Thus, a tunnel junction where both electrodes are either MISC or MASC ferromagnets exhibits negative tunneling magnetoresistance (TMR). This is observed in manganite tunnel junctions of identical materials separated by a thin STO insulating barrier [10, 11]. In contrast, for a tunnel junction with one MISC and one MASC ferromagnetic electrode the MR is positive. This has experimentally been observed in

$La_{0.7}Sr_{0.3}MnO_3$/STO/Fe_3O_4 tunnel junctions [12] showing large positive MR, where Fe_3O_4 is a MISC half-metallic ferrimagnet and $La_{0.7}Sr_{0.3}MnO_3$ is the MASC half-metallic ferromagnet. Here, we investigate the spin character of $La_{0.7}Ce_{0.3}MnO_3$ at E_F from the magnetotransport properties of the tunnel junction using the MASC ferromagnet $La_{0.7}Ca_{0.3}MnO_3$ as a spin analyzer.

Fig. 1(a) shows the magnetic field dependence of the current versus voltage $(I-V)$ curve across the tunnel junction measured in the CPP geometry at 300 K. We do not see a significant TMR, as expected, since at this temperature both $La_{0.7}Ce_{0.3}MnO_3$ and $La_{0.7}Ca_{0.3}MnO_3$ are paramagnetic semiconductors and the device behaves like a rectifying diode. However, in a field of 7.5 T the spin disorder scattering of a single layer is reduced, and the in-plane MR is quite large [1]. Fig. 1(b) shows the magnetic field dependence of the tunneling $I-V$ curve taken at 100 K, in zero field and in a field of 2 T. The magnetic field dependence of the $I-V$ curves (both positive and negative bias) clearly shows a bias dependent MR, i.e., below a threshold bias voltage (or current), we find a negative MR and above this a positive MR prevails. The field dependence of the $I-V$ curves taken at 48 K [Fig. 1(c)] does not show any bias dependence, exhibiting a positive MR at all voltages. In order to rule out any significant influence of the Nb-STO/$La_{0.7}Ce_{0.3}MnO_3$ bottom junction on the results of the tunnel junction we also deposited single layers of $La_{0.7}Ce_{0.3}MnO_3$ (and $La_{0.7}Ca_{0.3}MnO_3$) of identical thickness upon Nb-STO. As a main result, the MR of the Nb-STO/$La_{0.7}Ce_{0.3}MnO_3$ bottom junction is several orders of magnitude smaller compared to that of the FTJ and is always negative. Moreover, the $I-V$ curve of the former is highly asymmetric [inset Fig. 1(c)] down to the lowest temperature.

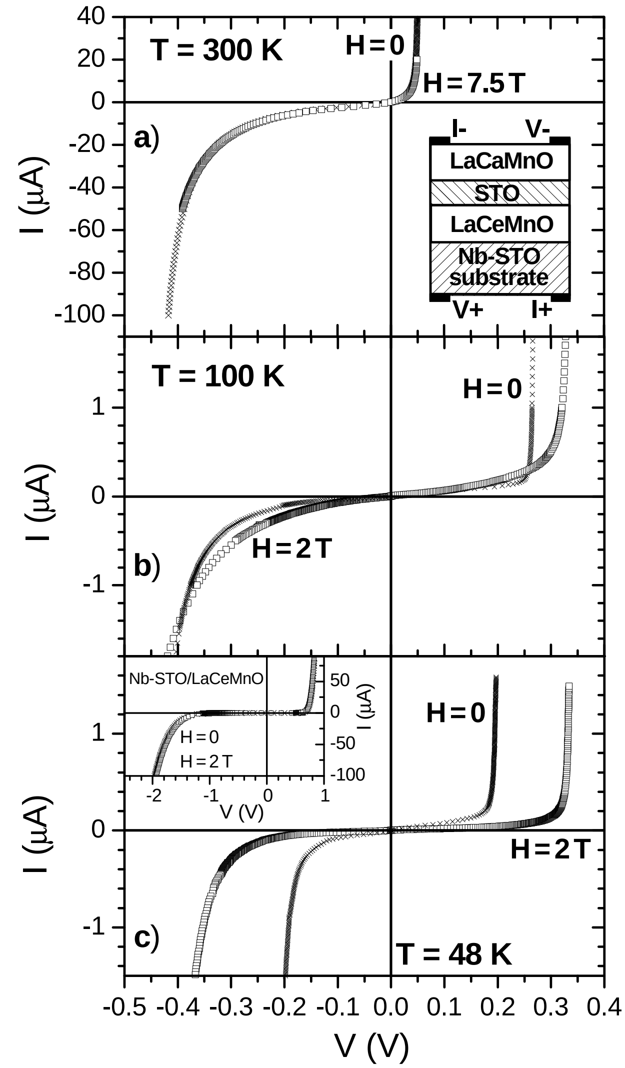

FIG. 1: (a) The tunneling $I-V$ characteristics of the $La_{0.7}Ce_{0.3}MnO_3$/STO/$La_{0.7}Ca_{0.3}MnO_3$ trilayer junction, taken at 300 K, in zero field and in an in-plane field of 7.5 T. Inset: layout of the multilayer device. (b) The same as before, taken at 100 K, in zero field and in a field of 2 T. (c) The same as above, at 48 K. Inset: $I-V$ curve of $La_{0.7}Ce_{0.3}MnO_3$ on Nb-STO at 48 K for comparison.

First we concentrate on the $I-V$ characteristics of the tunnel junction at the lowest temperature (48 K). Here, the positive TMR is intriguing. In hole doped manganites, three of the Mn-3d electrons form the localized t_{2g} band. The remaining electrons occupy the conducting e_g band which is energetically higher than the t_{2g} in a (nearly) cubic crystal field. The crystal field splitting energy is estimated to be $\Delta_{cf} \approx 1.8$ eV [1]. The e_g band splits further due to Jahn-Teller distortion into two sub-bands, e_g^1 and e_g^2, which are separated by the Jahn-Teller splitting energy, $\delta_{JT} \approx 1.2$ eV [1, 13]. Jahn-Teller distortion also causes a splitting of the t_{2g} band by δ_{JT}^*. Moreover, Hund's rule coupling removes the spin degeneracy in the ferromagnetic state. The resulting separation of the spin-up ($e_g\uparrow$) and spin-down ($e_g\downarrow$) bands is denoted by U_H whereas the separation of the $t_{2g}\uparrow$ and $t_{2g}\downarrow$ bands is labeled U_H^*. The Mn-3d spin dependent density of states (DOS) of $La_{0.7}Ca_{0.3}MnO_3$ at low temperature is sketched in Fig. 2(a). The bandwidth of the conducting e_g sub-bands is of the order of 1 eV [1]. U_H is estimated from band structure calculations to be of the order of 2 eV in the undoped compound—a value that may decrease with doping in the hole doped compound [14]. In hole doped manganites like $La_{0.7}Ca_{0.3}MnO_3$, which have 0.7 electrons in the e_g band, the conduction electrons predominantly occupy the lowest sub-band $e_g^1\uparrow$ and the hole doped manganite is consequently a MASC ferromagnet [Fig. 2(a)].

In $La_{0.7}Ce_{0.3}MnO_3$, there is clear evidence for electron doping on the Mn-site in *single* layer epitaxial films, e.g., from x-ray absorption spectroscopy [5]. Hence, the $e_g^1\uparrow$ sub-band is completely filled. For the remaining additional (doped) electrons two scenarios are possible: i) weak Hund's rule coupling $U_H^* < \Delta_{cf} + \delta_{JT}$ and ii) strong Hund's rule coupling $U_H^* > \Delta_{cf} + \delta_{JT}$. In the first case, $t_{2g}\downarrow$ is energetically lower than $e_g^2\uparrow$ and the former will

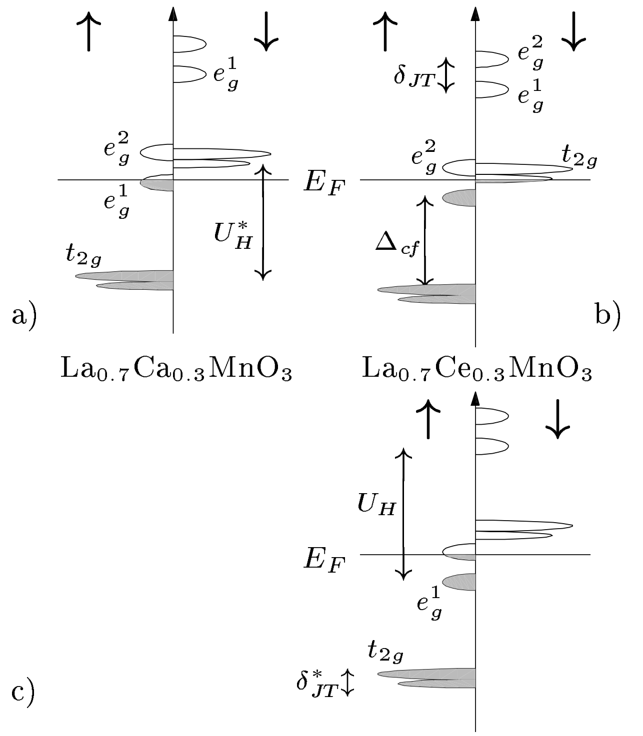

FIG. 2: Schematic diagram of spin dependent (large arrows) density of states of (a) the Ca and (b) and (c) the Ce-doped compounds at low temperature. For the Ce-doped compound, panel (b) [panel (c)] depicts the case of the level $t_{2g}\downarrow$ being energetically lower [higher] than $e_g^2\uparrow$ resulting in a MISC [MASC] state. Our tunneling experiments indicate MISC at E_F for $La_{0.7}Ce_{0.3}MnO_3$. For tunneling, panels (a) and (b) in the diagram correspond to the high field case, i.e., aligned magnetizations within the two ferromagnetic layers and hence, increased resistance due to opposite spin states at E_F. (See text for definitions of the energies.)

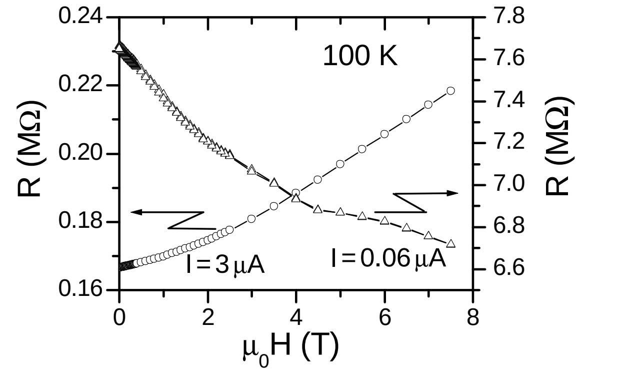

FIG. 3: Tunneling resistance (R) vs. magnetic field (H) at 100 K for two different bias currents $I = 0.06\,\mu$A and $3\,\mu$A.

get partially filled [Fig. 2(b)]. The compound will be a MISC ferromagnet in an intermediate spin state. In the second case, the remaining electrons will occupy the $e_g^2\uparrow$ sub-band resulting in a MASC ferromagnet in high spin state [Fig. 2(c)]. The observation of a positive TMR in $La_{0.7}Ce_{0.3}MnO_3$/STO/$La_{0.7}Ca_{0.3}MnO_3$ at low temperature definitely favors the first scenario with antiparallel spins at E_F for fields high enough to align the magnetizations within the two ferromagnetic layers [cf. Fig. 2(a) and (b)]. This result is supported by the known energy values given above if $U_H^* \approx U_H$ is assumed. Band structure calculations [13] also predict the near-degeneracy of the energy positions of the $e_g^2\uparrow$ and the $t_{2g}\downarrow$ sub-bands.

The minority spin character and the related intermediate spin state observed in $La_{0.7}Ce_{0.3}MnO_3$ are intriguing for several reasons. First, due to the usually large on-site Hund's rule coupling this is rarely observed in manganese compounds where Mn is in the divalent state including compounds such as MnO. Secondly, the transport and magnetic properties of the hole doped manganites are conventionally understood from this large on-site Hund's rule coupling in manganese and the electron-lattice coupling arising from the Jahn-Teller effect in Mn^{3+}. The ferromagnetic ground state in hole doped compounds like $La_{0.7}Ca_{0.3}MnO_3$ is driven by the double exchange interaction between Mn^{3+} and Mn^{4+}. This, however, is unlikely to be the dominant mechanism in $La_{0.7}Ce_{0.3}MnO_3$ if the manganese is in intermediate spin state. The striking similarity between the magnetic and transport properties of $La_{0.7}Ce_{0.3}MnO_3$ and its hole doped counterpart [3] raises questions anew regarding the origin of colossal MR in these compounds. It should be pointed out in this context that even in the hole doped compound the existence of Mn^{3+} and Mn^{4+} in the pure high spin state has been questioned recently. From point contact Andreev reflection measurements [15] the existence of minority spin carriers in the hole doped compound $La_{0.7}Sr_{0.3}MnO_3$ was concluded. Studies on tunnel junctions using a superconducting electrode and $La_{0.7}Sr_{0.3}MnO_3$ [16] also showed the polarization $P = (n_\uparrow(E_F) - n_\downarrow(E_F))/(n_\uparrow(E_F) + n_\downarrow(E_F))$ ($n_\uparrow$ and $n_\downarrow$ being the spin up and spin down DOS) to be of the order of 72%, which is much smaller than the polarisation expected for a half-metal [17]. Existing band structure calculations [18] predict an even lower spin polarization. These results indicate that the manganese is not in the pure high spin state in both electron and hole doped manganites with perovskite crystal structure. Therefore the general explanation of transport and magnetic properties of colossal MR manganites in terms of double exchange as the dominant mechanism needs a closer examination regardless of their high half-metallic transport character.

Fig. 3 shows the resistance versus field ($R - H$) of the tunnel junction at 100 K. At a very small bias current ($I = 0.06\,\mu$A) the MR is negative while at a large current ($I = 3\,\mu$A) the MR is positive. A description of the bias dependence of the MR at 100 K [Fig. 1(b)] and 200 K (not shown) is beyond the ground state picture described in Fig. 2. Here, a detailed knowledge of the band structure and the temperature evolution of the bands in $La_{0.7}Ce_{0.3}MnO_3$ would be required. Since at high bias

the large electric field across the insulating tunnel barrier shifts their Fermi energies considerably with respect to each other, we first concentrate on the temperature dependent TMR observed at low bias. The crossover of the TMR from positive to negative at low bias suggests a change in the dominant spin character of the ferromagnet at E_F with temperature. This could happen for two reasons. First, in transition metal oxides the interplay between competing energy scales can induce a crossover from one spin state to another with temperature. For example, in $LaCoO_3$ where the crystal field energy slightly exceeds the Hund's rule coupling energy, Co is in a low spin, effectively non-magnetic state at low temperature. Around 100 K the cobalt ions undergo a crossover from a low spin state to an intermediate/high spin state accompanied by a change in magnetic and electric properties [19]. Since the $t_{2g}\downarrow$ and $e_g^2\uparrow$ bands are at similar energy levels (and may even overlap) in the manganites, a temperature dependent crossover from an intermediate spin state to a high spin state cannot be ruled out in $La_{0.7}Ce_{0.3}MnO_3$. It may be caused, e.g., by decreasing Δ_{cf} with increasing temperature. This needs to be substantiated through other measurements. Secondly, even in the absence of such a crossover in the Mn spin state the dominant spin character of the carriers *at* E_F in a ferromagnet can change. For example, in a Stoner ferromagnet the exchange splitting between spin up and spin down bands decreases with increasing temperature, which changes the filling of the up and down spin bands. Therefore, subtle features in the DOS as a function of energy E can modify the relative ratio of up (e_g) and down (t_{2g}) spins at E_F without changing the overall spin state of the underlying Mn-ions.

We now focus on the bias dependence of the MR at 100 K and 200 K. A bias voltage V_b on a metallic tunnel junction shifts the Fermi levels of the two electrodes by eV_b. The tunneling of electrons across an insulating barrier, however, occurs at equal energy levels. Hence, the tunneling probabilities for the magnetization of the two electrodes parallel (antiparallel) to each other, $T_{\uparrow\uparrow}$ ($T_{\uparrow\downarrow}$), are given by

$$T_{\uparrow\uparrow} \;\propto\; n_\uparrow(E^+)\,n'_\uparrow(E^-) \;+\; n_\downarrow(E^+)\,n'_\downarrow(E^-)\;,$$
$$T_{\uparrow\downarrow} \;\propto\; n_\uparrow(E^+)\,n'_\downarrow(E^-) \;+\; n_\downarrow(E^+)\,n'_\uparrow(E^-)$$

respectively, where $E^+ = E_F + \frac{eV_b}{2}$ and $E^- = E_F - \frac{eV_b}{2}$. Here, $n_\uparrow(E)$ and $n_\downarrow(E)$ are the spin up and spin down DOS in $La_{0.7}Ca_{0.3}MnO_3$ and $n'_\uparrow(E)$ and $n'_\downarrow(E)$ are the corresponding ones in $La_{0.7}Ce_{0.3}MnO_3$. The relative magnitude of $T_{\uparrow\uparrow}$ and $T_{\uparrow\downarrow}$ depend on the details of the spin up and spin down DOS. At 100 K and 200 K, the negative MR at low bias voltage suggests that $T_{\uparrow\uparrow} > T_{\uparrow\downarrow}$ giving a negative MR. However, at the same temperatures, at large V_b the MR may change sign if this inequality is altered owing to features in the energy dependent DOS. Moreover, small changes in the relative energies of the $t_{2g}\downarrow$ and $e_g^2\uparrow$ bands due to V_b may change their occupancy which may result in a bias dependent crossover. Here, a detailed understanding can emerge only when the DOS in $La_{0.7}Ce_{0.3}MnO_3$ is known in sufficient detail.

In summary, we have reported the magnetotransport properties of a tunnel junction made of electron and hole doped manganites. The observed minority spin carrier transport in $La_{0.7}Ce_{0.3}MnO_3$ is of fundamental interest to understand the interplay of the Hund's rule coupling energy with other energy scales such as Jahn-Teller energy and crystal field energy in doped manganites. We believe that this result will motivate further studies of the exact electronic structure of both electron and hole doped manganites and may open up an alternative approach towards *spintronics*.

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